

DESCRIPTION

HIGH HYDROGEN ABSORBING ALLOY AND

METHOD FOR THE SAME

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[Claims]

10 [Claim 1] A hydrogen absorbing alloy, characterized
in that a thermal treatment is performed on an amorphous
alloy of a composition having atom% represented by com-
position formula: $Zr_{100-a-b}Pd_aM_b$, where $15 \leq a \leq 40$, $0 \leq b \leq 10$, M is
at least one species of Pt, Au, Fe, Co and Ni) in the atmosphere
or an oxygen atmosphere and the obtained Pd, Pd compound
or both of them is dispersed having ultrafine particles in
ZrO₂ mother phase.

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[Claim 2] A hydrogen absorbing alloy according to
claim 1, characterized in that a hydrogen absorbing amount
shows a Pd weigh ratio 2.5 weight% or more.

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[Claim 3] A hydrogen storage/transportation con-
tainer, characterized in that a hydrogen absorbing alloy
according to claim 1 or 2 is used as a hydrogen stor-
age/transportation medium.

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30 [Claim 4] A method for manufacturing a hydrogen
absorbing alloy according to claim 1, characterized in that
a melt bath of a mother alloy manufactured by melting is
rapidly solidified at a cooling speed of 10⁴K/s or more so
as to obtain an amorphous alloy, then a thermal oxidation
treatment is performed on it in the atmosphere or an oxygen
atmosphere at a temperature of 250 to 300 °C, an alloy element
Zr is selected and oxidized, and hydrogen absorbing metal
Pd or Pd compound is dispersed in ZrO₂ as ultrafine particles

having a nano-particle diameter.

[Detailed Description of the Invention]

[0001]

5 [Field of the Invention] The present invention
relates to: a hydrogen absorbing metal nano-ultrafine
particle dispersed hydrogen absorbing alloy using as a
precursor an amorphous Zr-Pd alloy or an alloy having at
least one species of Pt, Au, Fe, Co and Ni added thereto;
10 and a method for the same. In particular, the present
invention relates to the hydrogen absorbing alloy usable
as a hydrogen absorbing container having an excellent
hydrogen absorbing/releasing characteristic.

15 [0002]

[Prior Art] A variety of alloys such as Mm
(Mischmetall)-Ni system and Ti-V system is known as a hydrogen
absorbing alloy. Especially, Mm-Ni system and Ti-V system
are used for an electrode material of an electrical cell
20 and hydrogen storage. However, in the conventional hydrogen
absorbing alloys, there have been problems of causing an
insufficient capacity of an electrical cell in an electrode
material for the electrical cell and increasing a size of
a product for hydrogen storage due to a small hydrogen
25 absorbing amount.

[0003] As a method for increasing a hydrogen absorbing
amount, in addition to searching a new alloy, developing
a process for manufacturing a hydrogen absorbing alloy and
controlling a microstructures in a material are tried, for
30 example, by ultra finement/amorphousness of an alloy
structure by mechanical ironing, liquid rapid solidification
method and the like.

5 [0004] For example, as an alloy system, a well-known
Mg-Ni system is used. This alloy is caused to be amorphous
by the mechanical ironing. As a result, amorphous Mg-Ni
system hydrogen absorbing alloy capable of absorbing and
releasing hydrogen at a room temperature is developed, which
is, for example, disclosed in Japanese Laid-Open Publication
No. 11-61313 and Japanese Laid-Open Publication
No. 11-269572. Also, a hydrogen absorbing metal body only
10 including Pd metal micro particles is known (Japanese
Laid-Open Publication No. 04-311542). However, it is
pointed out that further break-through is required since
most of the amorphous hydrogen absorbing metals does not
have a plateau.

15 [0005] Moreover, a manufacturing method by a me-
chanical ironing or a mechanical grinding requires many hours
of mixing/alloying for production, thus resulting in a
problem of poor productivity.

20 [0006]
[Problems to be Solved by the Invention] An im-
provement of hydrogen absorbing characteristic is attempted
by causing a hydrogen absorbing metal/alloy to have fine
particle polycrystalline structure by the mechanical ironing
or the mechanical grinding. In view of these situations,
the present inventor(s) conducted an examination with
diligence in order to provide, as their objective, a hydrogen
absorbing metal nano-fine particle dispersed hydrogen
absorbing alloy having a microstructure for absorbing hydrogen
with higher efficiency; and a method for manu-
facturing the same.

[0007]

[Means for Solving the Problems] As a result, Zr-Pd alloy was prepared and the composition thereof was limited. Also, with the oxidation of the alloy, Zr in the alloy was selected and oxidized. Accordingly, a material was obtained, the material having a microstructure having ultrafine nano-particles of hydrogen absorbing metal Pd, which has been condensed and generated from the amorphous state, dispersed in the oxide ZrO_2 (zirconia). Further, the present inventor(s) found out that a hydrogen absorbing amount of this material is by far larger than a hydrogen absorbing amount (reference value) of Pd, the amount of which is the same as the weight of Pd contained in the material, and the hydrogen absorbing amount of the material shows Pd weight ratio 2.5 weight % or more. As such, the present inventor(s) completed the present invention.

[0008] That is, a first invention of the present invention is a hydrogen absorbing alloy, characterized in that a thermal treatment is performed on an amorphous alloy of a composition having atom% represented by composition formula: $Zr_{100-a-b}Pd_aM_b$, where $15 \leq a \leq 40$, $0 \leq b \leq 10$, M is at least one species of Pt, Au, Fe, Co and Ni) in the atmosphere or an oxygen atmosphere and the obtained Pd, Pd compound or both of them is dispersed having ultrafine particles in ZrO_2 mother phase.

[0009] Further, a second invention of the present invention is a hydrogen absorbing alloy described above, characterized in that a hydrogen absorbing amount shows a Pd weight ratio 2.5 weight% or more.

[0010] Still further, a third invention of the present

invention is a hydrogen storage/transportation container, characterized in that a hydrogen absorbing alloy described above is used as a hydrogen storage/transportation medium.

5 [0011] Still further, a fourth invention of the present invention is a method for manufacturing a hydrogen absorbing alloy described above, characterized in that a melt bath of a mother alloy manufactured by melting is rapidly solidified at a cooling speed of 10^4 K/s or more so as to obtain
10 an amorphous alloy, then a thermal oxidation treatment is performed on it in the atmosphere or an oxygen atmosphere at a temperature of 250 to 300 °C, an alloy element Zr is selected and oxidized, and hydrogen absorbing metal Pd or Pd compound is dispersed in ZrO_2 as ultrafine particles having
15 a nano-particle diameter.

 [0012] In a first embodiment of the present invention, Pd (atom%) is greater than or equal to 15 atom% and less than or equal to 40 atom%. If Pd is less than or equal to
20 15 atom% and greater than or equal to 40 atom%, the releasing amount of absorbed hydrogen is decreased, thus resulting in a no practical use. Further, Element M is added to Pd having a high absorbing capability in order to further improve the releasing performance. If the total elements Pd and M
25 (atom% a+b) is less than 15 atom% or greater than 50 atom%, the starting material prepared by a rapid solidification method does not have an amorphous state. Also, if a micro structure is changed due to a deviation from the optimal range of Pd amount, the releasing amount of the absorbed
30 hydrogen is decreased, thus resulting in no practical use.

 [0013] In the present invention, the starting material is prepared by the rapid solidification method.

Thus, an amorphous state without separation in the material can be obtained. The starting material is oxidized, and one of elements (Zr) is selected and oxidized with higher priority. As a result, amorphous element Pd is condensed, and Pd and Pd compound nano-particle diameter fine particles having clean difference interfaces without separation is generated and dispersed in a mother phase. Accordingly, it is not preferable that the starting material indicates crystallinity.

[0014] Further, in $ZrO_2 + Pd$ nano-ultrafine particle dispersed hydrogen absorbing alloy according to the present invention, Pd contributes mainly to the hydrogen absorption, and the Pd weight ratio hydrogen absorbing amount is greater than or equal to 2.5 weight% and is preferably greater than or equal to 3 weight%. In the material according to the present invention, the ZrO_2 mother phase fundamentally does not show the hydrogen adsorbing characteristic. Accordingly, the value of the amount of hydrogen absorption evaluated by the Pd weight in the material, from which the weight of ZrO_2 is subtracted, is the amount of the Pd weight hydrogen absorbing amount.

[0015] In the present invention, amorphous Zr-Pd system alloy starting material is not limited to that manufacturing method. However, it is preferable to manufacture the amorphous Zr-Pd system alloy starting material by rapidly solidifying it at a speed of $10^4 K/s$ or more by a liquid rapid solidification method (e.g., a single roll method, a double roll method, a gas atomizing method, a melt extraction method).

[0016] Next, a description will be given regarding

a hydrogen absorbing metal nano-ultrafine particle dispersed absorbing alloy according to the first invention of the present invention. First, a mother alloy is melted so as to have a targeted alloy composition. This melting is preferably performed in an arc melting furnace with an inactive atmosphere (e.g., argon) filled therein. Next, the manufactured mother alloy is re-melted, and thereafter, the melted bath is rapidly solidified at a cooling speed of 10^4K/s or more so as to manufacture a rapidly solidified alloy.

[0017] As such a method of rapidly solidifying at a cooling speed of 10^4K/s or more, a various liquid rapid solidification method, such as conventionally well-known single roll method, double roll method, gas atomizing method and rotating liquid spray method in rotating liquid, can be utilized. In the present invention, it is preferable to use the single roll method, which is relatively easy to manipulate the cooling speeding. If the cooling speed is slower than 10^4K/s , it is difficult to obtain the formation of amorphousness.

[0018] Further, the amorphous starting material manufactured by the method described above having a shape of foil, powder or wire is oxidized at a temperature of about 250 to 350 °C in the atmosphere or an oxygen atmosphere for 24 hours. The heating method is not limited to a particular one. Various methods having an excellent productivity can be used. However, since only Zr in the material is selected and oxidized and the oxidation of Pd and the others are significantly suppressed, it is not preferable to heat up o a high temperature of 400 °C or more.

[0019]

[Example] Next, the present invention will be specifically described with reference to examples and comparative examples.

5 Example 1 and Comparative Examples 1 and 2

Alloys having a variety of compositions shown in Table 1 were melted in an argon atmosphere using an arc melting furnace so as to manufacture mother alloys. Thereafter, rapidly solidified thin strips in a flat shape were
10 manufactured by the single roll method. In the single roll method, the thin strips were melted in the argon atmosphere using a nozzle made of quartz. Then, the thin strips were sprayed at 0.3kg/cm^2 on a copper roll having a diameter of 20cm and rotating at 4000rpm by using a nozzle made of quartz
15 having a hole of 0.3mm. They were rapidly solidified so as to obtain amorphous alloys having a width of 1mm and a thickness of $20\mu\text{m}$. Next, the amorphous alloys were oxidized at a temperature of about 280 to 350 °C in the atmosphere or an oxygen atmosphere for 24 hours. The obtained alloys were
20 broken into pieces with about $30\mu\text{m}$. Thereafter, a hydrogen absorbing amount was measured under a temperature of 50 °C and 150 °C. In this measurement, a gbeltz-type/PCT characteristic measurement device (manufactured by Suzuki Shokan) was used, and a hydrogen pressurization measurement
25 was conducted up to 5MPa. Prior to the hydrogen absorption, a phase was identified by an x-ray diffraction method in order to determine the presence of the separation of crystalline phase.

30 [0020]
 [Table 1]

	Composition of Starting material (at.%)	Hydrogen absorbing characteristic measured temperature (°C)	Hydrogen absorbing amount of entire material (wt.%)	Pd weight ratio hydrogen releasing amount (wt.%) #1	Pd weight ratio hydrogen releasing amount (wt.%) #2	Phase of starting material
Example 1	Zr65Pd35	150	0.71	2.19	0.54	Amorphous
Example 2	Zr65Pd35	50	0.84	2.58	1.33	Amorphous
Example 3	Zr65Pd30Ni15	150	0.71	2.30	1.21	Amorphous
Example 4	Zr65Pd30Ni15	50	0.78	2.51	1.57	Amorphous
Comparative Example 1	Zr50Pd50	150	0.45	0.96	0.32	Crystalline
Comparative Example 2	Zr50Pd50	50	0.59	1.26	0.61	Crystalline
Comparative Example 3	Zr70An30	150	0.04	0.09	0.09	Amorphous
Comparative Example 4	Pd Reference value)	150	0.65	0.65	0.65	Crystalline
Comparative Example 5	Pd Reference value)	50	0.69	0.69	0.69	Crystalline

#1) In Examples 3 and 4, Pd+Ni weight ratio hydrogen absorbing amount converted in Pd+Ni and also in Comparative Example 3, Au weight ratio hydrogen absorbing amount converted in Au weight ratio

#2) Difference between the maximum hydrogen absorbing amount at the maximum balancing hydrogen pressure, about 4.5MPa, of a device used and a remaining hydrogen absorbing amount after releasing the hydrogen

5 [0021] As can be appreciated from Table 1, in the case of using amorphous Zr-Pd alloys of Examples 1 and 2 and amorphous Zr-Pd-Ni alloys of Examples 3 and 4 as starting materials, a hydrogen absorbing amount of the entire materials is greater than or equal to 0.7wt.%. On the other hand, in the case of the starting materials of comparative Examples 1 to 3 (Comparative Examples 1 and 2 include Pd exceeding an amorphousness formation range of the starting materials, and in Comparative Example 3, Pd was replaced with Au, which does not have a hydrogen absorbing capability) deviating from a composition range of alloy according to the present invention, a hydrogen absorbing amount is smaller than that of Examples 1 to 4.

[0022] In the material according to the present invention, ZrO₂ mother phase fundamentally does not show the hydrogen adsorbing characteristic. Accordingly, the value

of the hydrogen absorbing amount evaluated by the Pd weight in the material, from which the weight of ZrO_2 is subtracted, is the Pd weight ratio hydrogen absorbing amount. When this value is used for comparison in Table 1, the Pd weight ratio hydrogen absorbing amount shows 2 wt.% or more in Examples 1 and 2. In contrast, the Pd weight ratio hydrogen absorbing amount shows less than 1.5wt.% in Comparative Examples 1, 2 and 3. Examples 1 and 2 show three to four times of absorption efficiency when compared to a hydrogen absorbing amount by single Pd in Comparative Examples 4 and 5. As such, it is appreciated that the hydrogen absorbing alloy nano-particle dispersed micro structure manufactured by the present invention has significantly improved the hydrogen absorbing capability inherently possessed by an alloy.

[0023] Moreover, in Examples 3 and 4, in which Ni was added as a third element in addition to Zr and Pd, a hydrogen absorbing amount is about the same as that of Examples 1 and 2. However, a hydrogen releasing amount of Examples 3 and 4 is superior to that of Examples 1 and 2 at every temperature. As such, by adding a third element having a relatively high hydrogen capability, it was confirmed that it is possible to manufacture a hydrogen absorbing alloy with a higher practical use.

[0024] Figure 1 shows an observed view of the structure of the material according to the present invention. (a) of Figure 1 shows a bright field image of nano-Pd particles dispersed in ZrO_2 mother phase by a transmission electron microscope. (b) of Figure 1 shows an electronic diffraction image. (c) of Figure 1 shows a dark field image obtained from a diffraction ring of the nano-Pd particles. Separation of Pd fine particles in ZrO_2 mother phase was observed using

the transmission electron microscope.

[0025]

5 [Effect of the invention] A hydrogen absorbing alloy
using an amorphous Zr-Pd-M (M=Pt, Au, Fe, Co, Ni) alloy
according to the present invention as a precursor has an
excellent hydrogen absorbing/releasing efficiency, and can
be applied to a various fields, especially, to a fixed hydrogen
10 absorbing equipment with preference. In addition, it can
be an indicator of a structure design for a material for
taking in hydrogen with efficiency. Further, instead of a
conventional mechanical ironing, the single roll method,
which is a simple method and capable of serial production,
is used to manufacture an amorphous Zr-Pd-M (M=Pt Au, Fe,
15 Co, Ni) alloy precursor and oxidize it, which made it possible
to obtain a highly efficient hydrogen absorbing alloy.

[Brief Description of the Drawings]

20 [Figure 1] is a picture in substitute for a diagram
showing a structure of an alloy of Example 1 as an image by a
transmission electron microscope.